Supporting Information

Xiang et al. 10.1073/pnas.1118338109

SI Text

Preparation of p-Si Wire-Array Photoelectrodes. To obtain patterned wire growth, p^+-Si (111) wafers with a resistivity of <0.001 Ω cm were coated with 300 nm of thermal oxide. A layer of S1813 photoresist (Rohm and Haas) was then deposited onto the oxide, and the photoresist was exposed through a chromium photolithography mask, followed by an oxide dry etch, to produce an array of 3 μm diameter holes on a 7 μm pitch square lattice. Buffered HF (Transene) was used to remove unmasked oxide before thermal evaporation of 350 nm of Cu (6N, Kurt Lesker) and subsequent lift-off.

The growth substrates were then cleaved into approximately 2 cm × 2 cm chips that were rinsed with acetone and isopropyl alcohol, and then introduced into a vapor-liquid-solid (VLS) chemical vapor deposition (CVD) growth chamber. The base pressure of the CVD chamber was <10 mTorr. The substrates were then annealed for 20 min in H_2 (g) (500 sccm) at 1,000 °C. Wire growth was performed at atmospheric pressure at 1,000 °C by introduction of a 500 sccm H_2 (g) carrier gas flow and a 50 sccm $SiCl_4$ (g) precursor gas flow. The dopant density of the wires was controlled by varying the flow rate of the in situ dopant, BCl_3. The length of the wires was controlled by varying the duration of the growth.

Following growth, the substrates were cooled slowly under H_2 (g) to 750 °C to allow the Cu VLS catalyst to diffuse out of the wires. The wires were then cooled under He to room temperature. The Cu VLS catalyst tips were removed by etching the samples for 30 min in 1.5 M $FeCl_3$ (aq), followed by etching for 10 s in 5.8 M HF (aq). The outer surface of the wire was etched in 8 M KOH (aq) for 1 min at room temperature.

Formation and Characterization of Ag Metal Films in the Internal Volume of p-Si Wire-Array Photoelectrodes. To produce films of Ag that were physically embedded into the internal volume of the Si microwire arrays, chips of p-Si wire arrays that were not mounted as electrodes were cleaved into approximately 1 cm × 1 cm squares. The wire-array samples were then thermally oxidized at 1,100 °C under O_2 (4,000 sccm) for 90 min, followed by electron-beam evaporation of >500 nm Al_2O_3 (99.99%, Kurt Lesker) over the entire sample. After masking off the edges of the device substrate with Kapton tape, a 5 nm Ti (99.99%, Kurt Lesker) adhesion layer, followed by a 200 nm film of Ag (99.99%, Kurt Lesker), was deposited by electron-beam evaporation.

The modified Si wire-array electrodes were etched in 2 M HNO_3(aq) for 3 s to remove residue Ag from the sidewalls of the Si microwires. The substrate area that had been previously masked off by Kapton tape was then covered with epoxy (Hysol 9460F, McMaster-Carr). Ohmic contact was made by scratching the back side of the substrate with Ga : In eutectic. Cu/Sn wire was then attached with conductive Ag paste to make an external back contact to the electrodes. Contact to the interdigited Ag film that was located between the Si microwires, as well as to the side of the oxide-isolated substrate, was made by affixing a Cu/Sn wire to the Ag by use of silver solder (McMaster-Carr). Both Cu/Sn wires were fed through the back of a supporting glass tube, and were sealed with epoxy (Hysol 9460F, McMaster-Carr) to prevent electrical shorting.

The photoactive area (approximately 0.5 cm × 0.5 cm) of wire-array substrates was prepared by scratching the wires off of the substrate with a ceramic-coated stainless steel razor blade. The area was determined by scanning the photoelectrodes with a commercially available scanner (Epson V300). A clear definition of the photoactive part of the wire array also served to prevent electrical shorting through the sides of the substrate.

Scanning electron microscope (SEM) images were collected using a field-emission SEM (Hitachi S-4100). Optical microscopy images were collected using an Olympus BX-51 microscope.

Nonaqueous Photoelectrochemistry. For all nonaqueous photoelectrochemical experiments, CH_3CN (anhydrous, 99.8%, Sigma Aldrich) was distilled under N_2 (g) (ultra-high purity, Air Liquide) from CaH_2 (≥97%, Fluka). Battery-grade $LiClO_4$ (anhydrous, 99.99%) was purchased from Sigma Aldrich, and was used as received. Battery-grade electrolyte solution (1.0 M $LiClO_4$ premixed in propylene carbonate, PC) was purchased from Novolyte Technologies, and was used as received. Bis(cyclopentadienyl) cobalt(II) (cobaltocene, $CoCp_2^0$) was purchased from Sigma Aldrich and was purified by sublimation. Bis(cyclopentadienyl) cobalt(III) hexafluorophosphate (cobaltocenium, $CoCp_2^+ \cdot PF_6^-$) was purchased from Sigma Aldrich and was recrystallized before use.

Current density vs. potential (J-E) data were collected at a scan rate of 40 mV s^{-1} using a Gamry (Reference 600) potentiostat. In addition to the working electrode, the electrochemical cell contained a stir bar, a Pt gauze electrode, and a Pt wire electrode that was allowed to equilibrate with the solution potential of the $CoCp_2^{+/0}$ redox couple. The stir bar was positioned adjacent to the photoelectrode and was rotated at approximately 3,000 rpm to facilitate mass-transport of the redox couple. The rotation of the stir bar was controlled with an external bar magnet that has been attached to an electric motor (NWSL 12270-9) driven by a DC power supply (Rail Power 1370). The electrochemical cell was contained inside a VAC Omni-Lab glovebox that had <0.5 ppm of O_2 (g). Air Mass (AM) 1.5 equivalent illumination was provided from a Sylvania ELH-type W-halogen lamp with a quartz diffuser. The light intensity was monitored by a Si photodiode that was placed at the same position in the electrochemical cell as the working electrode.